

Calcium-Oxide-Catalyzed Reactions of Hydrocarbons and of Alcohols

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Calcium oxides are catalysts for the double-bond isomerization of olefins, hydrogen disproportionation, dehydrogenation, and isomerization of 1,3- and 1,4-cyclohexadiene, dehydrogenation and hydrogen disproportionation of cyclohexene, hydrogenation of alkenes and of cyclohexene, dehydrogenation of alcohols, and hydrogen transfer between an alcohol and ketone. The reactions have been studied in a pulse microreactor mainly at 240–340° using helium as a carrier gas, or hydrogen in the case of the hydrogenation studies.

The activity of the calcium oxide catalysts depended on their methods of preparation. The most active catalysts were those prepared from calcium hydroxide and calcined at 500°. When the calcination was made at 900° the calcium oxide showed no catalytic activity towards the isomerization of olefins, the activity however could be restored when the catalyst was annealed at 500°. Another active calcium oxide catalyst was prepared from calcium carbonate which was calcined at 900–1000°.

The catalytic activity of calcium oxide has been reported in condensation reactions such as the formation of mesityl oxide from acetone. In the field of hydrocarbon conversions Turkevich and Smith (1) have studied various oxide catalysts for the isomerization of butenes and found that calcium oxide showed the lowest activity. Krylov and Fokina (2) have found that the dehydrogenation of cyclohexane at 0.2 mm of pressure and at 300–450° proceeded at a satisfactory rate. Nickels and Corson (3) have reported that calcium oxide, prepared by calcination of limestone, converted ethylnaphthalene to vinylnaphthalene at 650°.

Foster and Cvetanovic (4) studied the stereoselective isomerization of 1-butene to *cis*- and *trans*-2-butene over basic catalysts, including calcium oxide at 200°. Krylov and co-workers (5) have investigated the reaction of isopropyl alcohol

vapor over calcium oxide, calcium hydroxide, and calcium carbonate at 360–460°. The isopropyl alcohol underwent dehydration and dehydrogenation reactions. The authors concluded that the oxides are more active in the dehydrogenation than the carbonate.

Albeck *et al.* (6) have observed that limonene undergoes double-bond isomerization and dehydrogenation when passed over commercial calcium oxide at 375°.

The present study had been undertaken in order to determine the effect of the method of preparation of calcium oxide on its catalytic activity and to determine the scope of calcium oxide catalyzed reactions.

EXPERIMENTAL PROCEDURE

The reactions were studied in a pressure-micropulse reactor developed in this laboratory (7). The reactor which consisted of a 5½ inch long stainless steel tube with a 3/8-inch inside diameter was filled with 200 mg of catalyst of 400–600 μ, and sup-

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ported by a layer of 640- μ glass beads. The reactor consisted of an upper preheater section, catalyst section, and bottom-spacer section. The upper and lower sections were heated by means of cartridge heaters, while the center part was heated by a furnace consisting of two semicircular heating elements. The temperatures of the reactor assembly were controlled manually from a panel, the reactor furnace was controlled by an on-off temperature controller. Temperatures of the various parts of the reactor were measured with iron-constantan thermocouples.

Helium or hydrogen were used as carrier gases. They were purified over a high-pressure Deoxo catalyst (Engelhart Industries, Inc., Newark, New Jersey) and over a dryer containing molecular sieve. Generally a flow of 120 ml/min of either helium or hydrogen was passed through the reactor; 5 μ l of the compound under investigation was injected into the reactor through a silicon rubber septum.

The reactor was connected to an F & M Model 300 programmed temperature gas chromatograph (F & M Scientific Corporation, Avondale, Pennsylvania). The effluent of the reactor was trapped at liquid nitrogen temperature in a coil which was part of the lower section of the gas chromatographic column (?). The Dewar flask containing the liquid nitrogen was then removed, and a certain period of time, about 6 min, which was established experimentally, was allowed for this section of the column to warm up. After this period, the temperature programming was applied to the whole column.

The peak areas were determined by an electronic integrator with a print-out system (Infotronics Corporation, Houston, Texas).

The following chromatographic columns were used:

Column 1 was 10 m long, 1/4-inch outside diameter packed with Ucon 75H 90,000 polar deposited in 20% concentration on Chromosorb W, 60-80 mesh.

Column 2, the same size as column 1, was filled with silicon gum rubber, phenyl methyl ether GE-SE-52 in 15% concentration on Chromosorb W, 60-80 mesh.

Column 3 was 6 meters long, 1/4 inch

in diameter and contained 33% 2,4-dimethylsulfolane on fire brick Gas Pak P, 80-100 mesh.

Catalysts

The following catalysts were used:

Group 1. Commercial calcium oxide which, according to the manufacturer, was made by calcination of marble.

Group 2. The calcium oxide catalysts belonging in this group were prepared from calcium hydroxide which was calcined in a muffle furnace at temperature ranging from 400° to 1000°. On calcination virtually the theoretical amount of water was lost. The calcium hydroxide was obtained by reacting metallic calcium of over 99% purity with deionized water in a polyethylene flask. Care was taken to avoid contact with carbon dioxide and glass.

Group 3. The catalysts in this group were made from calcium carbonate, which was prepared by reacting calcium metal with water and carbon dioxide in a polyethylene flask. Any bicarbonate formed was decomposed by heating the material on a water bath. On calcination at 900° the theoretical amount of carbon dioxide was liberated, according to the loss of weight.

The list of catalysts is given in Table 1.

TABLE 1
CALCIUM OXIDE CATALYSTS

Catalyst no.	From	Calcination temp. ^a (°C)
1	Ca(OH) ₂	500°
2	Ca(OH) ₂	650°
3	Ca(OH) ₂	800°
4	Ca(OH) ₂	900°
5	Ca(OH) ₂	900° ^b
6	CaCO ₃	900°
7	Ca(OH) ₂	400°

^a The catalysts were calcined for 1-2 hr at the indicated temperature.

^b The catalyst was heated at 500° for 1.5 hr in a flow of helium.

RESULTS

Commercial Calcium Oxide

Preliminary experiments were made with a commercial calcium oxide catalyst. This

catalyst showed activity for the migration of the double bond in 1-hexene at 320–340°, the extent of isomerization was 10–15%. The commercial calcium oxide catalyzed the dehydration at 309° of *tert*-butyl alcohol to isobutylene with a yield of 48%. When 20 μ l of pyridine was passed at 320° over the catalyst prior to the injection of *tert*-butyl alcohol the yield of isobutylene produced dropped to 15% and that of 1-hexene to 2-hexenes to about 2%. Regeneration of the catalyst with air restored the dehydrating activity of the catalyst to 27%.

Isomerization of Alkenes

1-Hexene was chosen as a model compound for the study of double-bond isomerization of alkenes. The experimental results are given in Table 2. A blank experiment which was made with only glass beads in the reactor, showed no isomerization under the optimum experimental condition given in Table 2.

Two types of calcium oxide catalysts were used: one type was prepared from calcium hydroxide by calcination at tem-

TABLE 2
ISOMERIZATION OF 1-HEXENE^a

Expt.	Catalyst	Temp. (°C)	Analytical column ^b	Isomerization (%)	Composition of isomerized hexenes (%) Peak—		
					1	2	3
1	Glass beads	346°	3	0	—	—	—
2	1	260°	3	76	0	67	33
3	1	340°	3	94	18	56	26
4	1 ^c	342°	3	74	0	65	35
5	2	340°	1	25	—	—	—
6	3	343°	1	0	—	—	—
7	4	348°	1	0	—	—	—
8	5	341°	1	91	76	24	0
9	5 ^d	340°	1	91	75	25	0
10	6	343°	3	89	12	50	38
11	6 ^e	351°	1	92	75	25	0
12	6 ^f	339°	1	91	75	25	0
13	6 ^g	346°	1	70	57	43	0
14	6 ^h	347°	1	0	—	—	—
15	1 ⁱ	340°	3	94	18	56	26
16	1 ^j	340°	3	85	—	—	—
17	6 ^k	340°	—	43	—	—	—
18	6 ^l	340°	—	89	—	—	—

^a The flow of helium through the reactor was 120 ml/min.

^b The relative retention times of hexenes were reported by S. Csicsery and H. Pines, *J. Chromatography* **9**, 38 (1962). On Column 3 they were as follows: 1-hexene, 1.57; *trans*-3-hexene, 1.65; *trans*-2-hexene, 1.76; *cis*-3-hexene, 1.76; *cis*-2-hexene, 1.9. Accordingly, the first peak after 1-hexene would be *trans*-3-hexene, the second unresolved *trans*-2- and *cis*-3-hexene, and the third *cis*-2-hexene. Column 1 gave two peaks, besides the peak for 1-hexene; the structure of the isomers corresponding to these two peaks were not determined.

^c The catalyst was used in many experiments prior to this experiment.

^d Same catalyst as in Expt. 8; two injections of 1-hexene were made between the two experiments.

^e The catalyst was heated at 500° for 1 hr in the presence of a current of helium.

^f The catalyst was heated as above in the current of equal volume of oxygen and nitrogen.

^g 100 μ l of purified 1-hexene was passed over the catalyst prior to the experiment.

^h 100 μ l of 1-hexene which was not purified from peroxides was passed over the catalyst from Expt. 13.

ⁱ 50 μ l of pyridine was passed over the catalyst.

^j 20 cc of ammonia was passed over the catalyst.

^k 20 μ l of pyridine was passed over the catalyst.

^l 20 μ l of pyridine was passed over the catalyst which was heated to 450° in a flow of helium.

peratures ranging from 500° to 900°, and the other type was made by calcining calcium carbonate at 900°.

Catalyst 1, which was produced from calcium hydroxide and calcined at 500°, showed good catalytic activity for the double-bond isomerization of 1-hexene. At 260° the extent of isomerization was 76% while at 340°, 94% of 1-hexene was converted to a mixture of 2- and 3-hexenes. At the lower temperature 3-hexenes were not formed; this is shown in the gas chromatogram by the absence of peak 1, corresponding to *trans*-3-hexene. These results indicate that the isomerization of 1-hexene to 3-hexenes is a stepwise reaction.

At the higher temperature with fresh catalyst, Expt. 3, the composition of the hexenes was close to the equilibrium mixture. The composition of the hexenes, including 1-hexene, was 1-hexene, 6%; *trans*-3-hexene (peak 1), 17%; unresolved *trans*-2- and *cis*-3-hexene (peak 2), 53%; and *cis*-2-hexene (peak 3), 24%. The calculated equilibrium mixture at 600°K given by Rossini and co-workers (8) and based on the heat of combustion is about 7/23/40/10/20 for 1-/*cis*-2-/*trans*-2-/*cis*-3-/*trans*-3-hexene. The calcium oxide catalyst underwent deactivation with time (Expt. 4). After repeated use, the extent of isomerization dropped from 94% to 74% and at the same time 3-hexenes were not formed.

Calcium oxide catalysts produced from calcium hydroxide were sensitive to the temperature at which they were calcined. When the temperature of calcination was raised from 500° to 650°, Catalyst 2, the conversion of 1-hexene to isomeric hexenes

dropped from 94% to 25% (Expt. 3 vs. Expt. 5). Calcium hydroxide calcined at 800° and 900° did not show any catalytic activity. However the catalytic activity can be restored if this material is annealed at 500° for 1.5 hr in a flow of helium, Expts. 8 and 9. The activity of this calcium oxide, Catalyst 5, is comparable with Catalyst 1, which has not been subjected to this high temperature of calcination.

The difference in the catalytic activity of calcium oxides prepared by calcination at 900° of calcium carbonate and calcium hydroxide, respectively, could be attributed to the difference in dislocations of the crystals (9) of the calcium oxides, which depend on the starting material from which they were prepared.

Pentenes were also subjected to isomerization at 250–260° over Catalyst 1, Table 3. Of the four pentenes studied, 1-pentene isomerizes most easily, 50% conversion; next 3-methyl-1-butene, 31% conversion. 2-Methyl-1-butene and 2-methyl-2-butene isomerized to the extent of 7% and 11%, respectively.

Unlike calcium oxides prepared from calcium hydroxide, the calcium oxide produced from calcium carbonate and calcined at 900° was a very effective catalyst for the isomerization of 1-hexene (Expt. 10). The extent of conversion and the composition of hexenes is similar to Expt. 3. The annealing of this catalyst at 500° for 1 hr either in a stream of an equimolar mixture of oxygen and nitrogen or in a stream of helium, did not alter its catalytic activity (Expts. 11 and 12).

Ammonia and pyridine, when passed

TABLE 3
ISOMERIZATION OF PENTENES OVER CALCIUM OXIDE PREPARED FROM CALCIUM HYDROXIDE^a

Expt.	Compound	Temp. (°C)	Isomerization (%)	Composition isomerized pentene ^b (%)	
19	1-Pentene	251°	50	<i>cis</i> -2-C ₅ H ₁₀	52
				<i>trans</i> -2-C ₅ H ₁₀	48
20	2-Me-1-butene	256°	7	2-Me-2-C ₄ H ₈	100
21	2-Me-2-butene	250°	11	2-Me-1-C ₄ H ₈	100
22	3-Me-1-butene	280°	31	2-Me-1-C ₄ H ₈	16
				2-Me-2-C ₄ H ₈	84

^a Fresh Catalyst 1 was used in each experiment.

^b Gas chromatographic column 3, containing sulfolane, was used.

over the catalyst prior to the injection of 1-hexene, did not seem to alter the catalytic activity of calcium oxide, Catalyst 1. There was however some deactivation of the catalyst when pyridine was injected over Catalyst 6. This deactivation was not permanent inasmuch as the catalyst could be reactivated with a stream of helium passed over it at 450°.

The activity of calcium oxide catalysts dropped considerably when 1-hexene containing peroxides was passed over them. For that reason caution had to be exercised to remove any traces of peroxides from 1-hexene, prior to passing it over the catalyst.

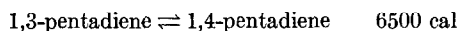
Hydrogen Disproportionation and Dehydrogenation

The title reactions were studied with 1,3- and 1,4-cyclohexadiene and cyclohexene as model compounds.

1,3- and 1,4-Cyclohexadiene. These hydrocarbons underwent isomerization, dehydrogenation, and hydrogen transfer reactions when passed over calcium oxide catalysts at 240° to 288° (Table 4). Small amounts of cyclohexene and relatively large amounts of benzene were produced, while cyclohexane was absent. The composition of the product indicates that the bulk of benzene must







have been produced by a dehydrogenation reaction with the liberation of hydrogen. The ratio of 1,3-/1,4-cyclohexadiene was in all the experiments equal to about 2.93, which is about the equilibrium constant for these two hydrocarbons at 286° ± 2°C.

The equilibrium mixture of the cyclohexadienes was established at 320° using a mixture of the two isomers, one of which was in an excess over the assumed equilibrium value. Starting with 1,3-/1,4-cyclohexadiene ratios of about 2.5 and 3.5, the ratios after the reaction were 2.87 and 2.99, respectively. The results differ very little from those obtained at 280°, which indicates that the enthalpy of isomerization, which was calculated to be 5200 cal, is smaller than that of the nearest reported analog, namely, 1,3- and 1,4-pentadiene, which is



The presence of peroxides affects the activity of the catalyst. The purified cyclohexadienes used in Expts. 24, 25, and 28 were stored for several months in a bottle without taking precautions to avoid their peroxidation, and as a result of it the conversion dropped considerably when these hydrocarbons were passed over calcium oxide. The deactivation was especially notable with respect to the dehydrogenation of the cyclohexadienes to benzene.

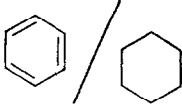
TABLE 4
REACTION OF 1,3- AND 1,4-CYCLOHEXADIENE OVER CALCIUM OXIDE

Expt.	Temp. (°C)	Catalyst	Analytical column	Conversion (%)	Composition of converted hydrocarbons (%)				Ratio  / 
									
<i>1,3-Cyclohexadiene</i>									
23	240°	5	1 ^a	97	23	3	0	74	—
24	286°	1	3	39 ^b	1	64	22	13	2.92
25	288°	1	3	30 ^b	1	69	24	6	2.96
<i>1,4-Cyclohexadiene</i>									
26	244°	5	1 ^a	92	8	—	—	92 ^a	—
27	280°	5	1 ^a	99	18	1	—	81 ^a	—
28	284°	1	3	82 ^b	16	60	—	24	—

^a Column 1 did not differentiate between benzene and cyclohexane. In view of the absence of cyclohexane in Expts. 24, 25, and 28, analyzed on column 3, it is assumed that the same must hold for the other experiments.

^b The cyclohexadiene, after purification, was stored for several months in the absence of an inhibitor, and then the samples were exposed to air and thus peroxidized.

TABLE 5
 REACTION OF CYCLOHEXENE^a

Expt.	Temp. (°C)	Conversion (%)	Composition of reacted product ^b (%)		Ratio 
			Cyclohexane	Benzene	
30 ^c	238°	55	40	60	1.5
31 ^d	242°	73	38	62	1.6
32 ^e	240°	62	39	61	1.6
33 ^f	237°	46	41	59	1.4
34 ^c	342°	56	20	80	4.0
35 ^d	339°	68	19	81	4.3
36 ^g	244°	16	31	69	2.1
37 ^h	244°	2	—	—	—
38 ⁱ	244°	13	38	62	1.6

^a Catalyst 5 was used.

^b VPC column 2, Ucon on Chromosorb, which was employed resolves benzene and 1,4-cyclohexadiene. Since 1,4-cyclohexadiene was absent it was assumed that 1,3-cyclohexadiene was also absent.

^c Cyclohexene was treated with ferrous sulfate·7H₂O to remove peroxides.

^d The purified cyclohexene was shaken with molecular sieve to remove traces of water and other impurities.

^e The cyclohexene was shaken with water before injection.

^f The cyclohexene was exposed to air and shaken for 15 min before injection.

^g Cyclohexene was stored in a bottle for an indefinite period of time; it contained peroxides.

^h This experiment followed Expt. 36, cyclohexene used was the same as in Expt. 36.

ⁱ Cyclohexene used was the same as in Expt. 30; this experiment followed Expt. 37.

Cyclohexene. The experimental results are given in Table 5. Catalyst 5 was used, which was prepared from calcium hydroxide, calcined at 900° and annealed at 500°. The cyclohexene, which was purified from hydroperoxides formed on storage, underwent hydrogen disproportionation and dehydrogenation, when passed over calcium oxide catalyst at 238°; cyclohexane and benzene were formed, Expt. 30. The dehydrogenation was the predominant reaction inasmuch as the ratio of cyclohexane to benzene produced was 1 to 1.5. The cyclohexene was purified by treating it at room temperature with ferrous sulfate, FeSO₄·7H₂O, and a few drops of sulfuric acid, washing, and distilling it. The subsequent shaking of the cyclohexene with molecular sieve had a beneficial effect on the reaction, and the conversion to cyclohexane and benzene increased to 73% (Expt. 31). Traces of water seem to have little effect upon the reaction (Expt. 32). However, shaking the same cyclohexene with air produced an adverse effect, and the conversion dropped to 46% (Expt. 33). The increase of tempera-

ture from 240° to 340° favors the dehydrogenation in preference to the hydrogen transfer reaction, and the ratio of benzene to cyclohexane produced was 4 to 1 (Expts. 34 and 35). Cyclohexane at these temperatures does not undergo dehydrogenation.

Stored cyclohexene which contained peroxides, deactivated the catalyst very rapidly, the conversion dropped to 16% and on second injection it dropped to less than 2%, (Expts. 35 and 37). The catalyst was also permanently deactivated since a purified cyclohexene, which was passed over this catalyst, gave only 13% conversion (Expt. 38).

The ratio of benzene to cyclohexane produced depended greatly on the temperature at which the reaction is made, and it ranged from 1.3 to 4.1 at 202°, 238°, and 342°, respectively.

Reactions in a Current of Hydrogen

1-Hexene, cyclohexene, and methylbutenes were injected in the presence of a current of hydrogen over calcium oxide catalysts Tables 6 and 7.

TABLE 6
REACTIONS OF 1-HEXENE AND OF CYCLOHEXENE IN A CURRENT OF HYDROGEN^a

Expt.	Temp. (°C)	Catalyst	Conversion (%)	Hydrogenated product	Composition of converted product ^b	
					Olefin. Peak—	
					1	2
<i>1-Hexene^c</i>						
39	155°	1	37	68	27	5
40	204°	1	65	57	29	14
41 ^d	201°	1	22	50	36	14
42 ^e	260°	1	18	33	45	22
43 ^f	252°	1	52	42	39	19
44 ^g	248°	1	57	47	37	16
45 ^h	250°	1	50	42	40	18
46 ^f	255°	1	62	29	44	27
47 ⁱ	247°	6	17	47	47	6
48 ^j	255°	6	61	5	39	56
49 ^k	340°	6	74	1	65	34
<i>Cyclohexene</i>						
50	151°	1	11	100	—	—
51	204°	1	13	100	—	—
52 ^l	256°	6	1	—	—	—
53 ^m	341°	6	<1	—	—	—

^a The flow of hydrogen was 120 ml/min.

^b Column 3, containing sulfolane, was used.

^c The 1-hexene was purified with FeSO₄·7H₂O.

^d After several experiments with cyclohexene.

^e Catalyst from Expt. 41 was used.

^f The catalyst was regenerated at 500° for 1 hr with a mixture of equal volumes of oxygen and nitrogen.

^g Catalyst from Expt. 43 was used.

^h After several experiments with 3-methyl-1-butene.

ⁱ After several experiments with cyclohexene.

^j The catalyst was heated for 1 hr at 500° in the presence of a current of hydrogen.

^k Catalyst from Expt. 48 was used.

^l This catalyst was heated at 500° for 1 hr in a current of hydrogen, 120 cc/min. It was used subsequently in Expt. 48.

^m This reaction was made following Expt. 49.

TABLE 7
REACTIONS OF METHYLBUTENES IN A CURRENT OF HYDROGEN^a

Expt.	Methylbutene injected	Temp. (°C)	Hydrogen flow (cc/min)	Conversion (%)	Composition of converted product (%)			
					Isopentane	2-Me-1-C ₄	2-Me-2-C ₄	3-Me-1-C ₄
54	2-Me-1-C ₄ ^b	253°	50	19	52	—	47	<1
55	2-Me-2-C ₄	253°	50	5	42	52	—	6
56	3-Me-1-C ₄ ^c	253°	120	68	60	3	37	—
57	3-Me-1-C ₄	250°	50	92	50	2	48	—

^a Catalyst 3, obtained from calcium hydroxide, was used. The product was analyzed on a sulfolane column.

^b 2-Methyl-1-butene.

^c 3-Methyl-1-butene.

1-Hexene underwent both hydrogenation and isomerization over Catalyst 1. The extent of hydrogenation was temperature-dependent, it dropped from 68% to 57% and to 42% as the temperature was raised from 155° to 204° and to 252°, respectively (Expts. 39, 44, and 46). The decrease in the rate of hydrogenation could best be interpreted as a more rapid double-bond migration of 1-hexene to 2- and 3-hexenes which are not as readily hydrogenated as the terminal olefin.

Calcium oxide which was prepared from calcium carbonate, Catalyst 6, was not very effective for the hydrogenation of olefins; it was, however, an excellent catalyst for the double-bond isomerization of 1-hexene (Expts. 48 and 49).

It was observed that partial hydrogenation of 1-hexene had occurred by the hot detector block of the gas chromatographic apparatus. For that reason the experiments with the olefins were made using a cold block.

The rate of hydrogenation of cyclohexene in the presence of Catalyst 1 was very slow and almost negligible in the presence of Catalyst 6, Table 6.

The hydrogenation of the three isomeric methylbutenes was investigated using Cata-

lyst 3, Table 7. The relative rate of hydrogenation of 3-methyl-1-/2-methyl-1-/2-methyl-2-butene was about 69/15/1 (Expts. 57, 54, and 55), respectively. There was also a preferential and a reversible isomerization of 2-methyl-1- and 2-methyl-2-butene. The isomerization was a stepwise reaction since 3-methyl-1-butene produced 2-methyl-2-butene with only a small amount of 2-methyl-1-butene (Expts. 56 and 57).

Reaction of Alcohols

Various alcohols were injected over calcium oxide catalyst in the presence of helium as carrier gas (Table 8). *tert*-Butyl alcohol underwent only 4% conversion in the presence of Catalysts 1 or 5. 2-Phenyl-2-propanol under similar conditions dehydrated to the extent of 64% to form α -methylstyrene. 2-Phenylethanol was 12% converted to styrene and β -phenylacetaldehyde.

Secondary and primary alcohols underwent only dehydrogenation to form ketones and aldehydes, respectively. The effect of the temperature of calcination of calcium hydroxide upon the dehydrogenation of pinacolyl alcohol was evaluated. It was again confirmed, as in the case of isomerization of

TABLE 8
REACTION OF ALCOHOLS

Expt. ^a	Alcohol	Temp. (°C)	Catalyst	Conversion (%)	Product
58	<i>tert</i> -Butyl	318°	7	2.2	Isobutylene
59	<i>tert</i> -Butyl	319°	1	4.3	Isobutylene
60	<i>tert</i> -Butyl	321°	3	2.2	Isobutylene
61	<i>tert</i> -Butyl	320°	4	0.4	Isobutylene
62	<i>tert</i> -Butyl	320°	5	4	Isobutylene
63	<i>n</i> -Butyl	342°	1	10	Butyraldehyde
64	<i>sec</i> -Butyl	324°	1	21	2-Butanone
65	<i>iso</i> -Butyl	325°	1	7	Isobutyraldehyde
66	2-Phenylethanol	342°	1	12	3% Styrene, 97% 2-phenylacetaldehyde
67	2-Phenyl-2-propanol	318°	1	64	α -Methylstyrene
68	Pinacolyl	319°	7	15	Pinacolone
69	Pinacolyl	320°	1	35	Pinacolone
70 ^b	Pinacolyl	325°	1	23	Pinacolone
71	Pinacolyl	337°	3	15	Pinacolone
72	Pinacolyl	319°	4	10	Pinacolone
73	Pinacolyl	320°	5	25	Pinacolone

^a The flow of helium was 120 ml/min.

^b The catalyst was extensively used prior to this reaction.

olefins that calcium hydroxide, which was calcined at 500° or at 900° and then annealed at 500°, was the most effective catalyst for the dehydrogenation of alcohols. It is interesting to note that Catalyst 4, which was calcined at 900° and which did not isomerize 1-hexene (Table 1, Expt. 7), was still able to dehydrogenate pinacolyl alcohol to the extent of 10%.

TABLE 9
HYDROGEN TRANSFER IN 2-PROPANOL
AND 2-BUTANONE

Expt. ^a	Temp. (°C)	% Conversion of	
		iso-PrOH → acetone	2-Butanone → 2-Butanol
74	312°	40	46
75 ^b	320°	40	52
76 ^b	319°	38	48

^a Equimolar quantities of 2-propanol and 2-butanone were employed. Catalyst 5, prepared from calcium hydroxide, was used. The chromatographic analysis was made on a Ucon column. The yields were based on peak areas; no correction factors were applied.

^b Four injections were made between this experiment and the preceding experiment.

Hydrogen transfer had occurred when a mixture of isopropyl alcohol and butanone were passed over calcium oxide at about 320°; both acetone and butanol were pro-

duced (Table 9). 2-Propanol at the same temperature practically did not undergo dehydrogenation.

Isomerization of 1-Hexene in a Flow System

All the experiments discussed above were made in a pulse reactor with a non-steady-state catalyst. In order to compare a non-steady-state with a steady-state catalyst a flow-type experiment was made in which 1-hexene was passed continuously over the calcium oxide catalyst in the presence of a current of helium. The reactor tube was the same as used in the pulse system; the flow of helium was adjusted in order to have conditions approximating those of the pulse reactor. The 1-hexene was thoroughly purified from any traces of peroxides and dried over molecular sieve. The 1-hexene was fed through the reactor by means of an adjustable micro-displacement pump of a design developed in this laboratory.

The reactor was connected to the gas chromatograph through a remote control pneumatically operated sampling device. Samples were introduced periodically into the gas chromatograph for analysis. The experimental conditions used and the results obtained are given in Table 10.

The experimental data showed very good agreement between the results obtained in

TABLE 10
ISOMERIZATION OF 1-HEXENE IN A FLOW SYSTEM^a

Run no.	Temp. (°C)	Total time on stream ^b	Conversion (%)	Composition of isomerized hexenes. Peak ^c —		
				1	2	3
1	340°	2 min	92.8	22.6	56.1	21.3
2	340°	1 hr	92.3	22.4	65.2	21.4
3	340°	2 hr	92.3	22.4	55.6	22.0
4	340°	3 hr	92.9	21.8	56.1	22.1
5	340°	4 hr	92.6	21.6	55.7	22.7
6	260°	5 hr	67.8	2.8	35.3	61.9
7	260°	6 hr	65.2	1.9	35.7	62.4
8	300°	8 hr	50.2	—	37.5	62.5
9	335°	9 hr	58.9	1.0	38.5	60.5
10	340°	10 hr	57.2	—	37.3	62.7
11	340°	12 hr	56.3	—	36.7	63.3

^a Catalyst: CaO produced from Ca(OH)₂ calcined at 550° for 2 hr, 400 mg. Feed: 2 ml/hr of 1-hexene and 80 ml/min of helium were passed through the catalyst.

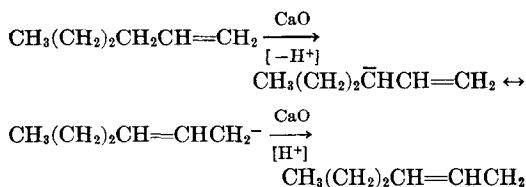
^b Time at which a sample was introduced into the chromatograph for analysis.

^c The analyses were made on a dimethylsulfolane column (Column 3); see Table 2, footnote b.

a pulse reactor and in the flow system (Table 2, Expt. 2 and Table 10, Runs 1-5). During the first 5 hr on stream at 340° the composition of the *n*-hexenes formed was approaching the thermodynamic equilibrium values. At the end of 12 hr of continuous run the activity of the catalyst diminished to cause only 56% isomerization of 1-hexene to *cis*- and *trans*-2-hexene but not to 3-hexenes.

DISCUSSION OF RESULTS

The main purpose of the present study was to determine the scope of hydrocarbon reactions catalyzed by calcium oxides. The starting material from which the calcium oxides were produced and the temperature of calcination determine the activity of the catalysts. The most active catalysts for the double-bond isomerization of 1-hexene were those prepared from calcium hydroxide and either calcined at 500°, or calcined at 900° and then annealed at 500°, and from calcium carbonate calcined at 900° (Table 1). Bases such as ammonia and pyridine do not seem to deactivate the catalyst. The isomerization of 1-hexene proceeded most likely by a mechanism involving an anionic allylic intermediate, similar to a mechanism postulated for a base-catalyzed isomerization of alkenes (11). The isomerization of 1-hexene to 3-hexene occurs stepwise, at first *cis*- and *trans*-2-hexene are produced, and then the 2-hexenes are readsorbed on the catalyst and isomerize to 3-hexenes. At low conversion only 2-hexenes are formed. The mechanism can be presented as follows



Although the isomerization seems to be of an anionic character, the relative rates of isomerization of pentenes, as given in Table 3, are not in accord with those reported from the isomerization of alkenes in the presence of potassium *tert*-butoxide in dimethyl sulfoxide (12, 13). From the ease of formation of the anions, namely, the

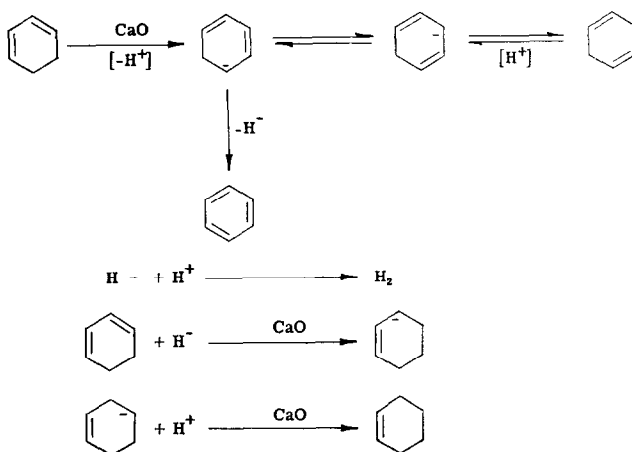
primary being produced more readily than the secondary and the latter more readily than the tertiary, it would be expected that 2-methyl-1- and 2-methyl-2-butene would isomerize faster than 3-methyl-1-butene, which was not the case. 1-Pentene isomerized the fastest, as expected.

Calcium oxide catalysts are sensitive to deactivation by organic peroxides which may be present in the olefins and therefore care had to be taken to remove all traces of peroxides from the olefins. This was accomplished by treating the olefins with ferrous sulfate. However, methylbutenes samples labeled 99% pure were purchased and used as such without further purification. It is possible therefore that the discrepancy between the expected and the observed rates of isomerization of methylbutenes could be attributed to some traces of peroxides present in the olefins.

1,3- and 1,4-Cyclohexadiene underwent a reversible isomerization, hydrogen disproportionation, and dehydrogenation. With freshly purified cyclohexadienes, benzene and cyclohexene were the main reaction products, the former predominating; cyclohexane was not formed. The presence of peroxides in cyclohexadienes deactivated the hydrogen disproportionation and dehydrogenation reaction, but did not seem to affect the isomerization. A similar observation had been reported in the case of limonene (6). The reaction occurring with cyclohexadienes is very similar to that encountered with sodium-organosodium-catalyzed reaction of cyclic diolefins, such as limonene and α -phellandrene (11, 14). The disproportionation reaction can be explained by diagram on p. 157.

The addition of a hydride to cyclohexene does not proceed too readily because the cyclohexyl anion is not stabilized by the allylic double bond (11).

Cyclohexene underwent disproportionation to benzene and cyclohexane over calcium oxide at about 240°. The ratio of benzene to cyclohexane formed was approximately 1.5 at 240° and 4.1 at 340°, which indicates that the dehydrogenation was the main reaction. Cyclohexane under similar conditions does not undergo dehydro-



genation. Although the formation of cyclohexane from cyclohexene through a transfer of a hydride should be a difficult reaction because of the relative instability of a secondary resonance nonstabilized anion, nevertheless similar reactions have been reported from this laboratory. Ethane, propane, and isobutane were by-products of side-chain alkylation of alkyl aromatics by means of strong bases (11).

Calcium oxide was found to be a hydrogenating catalyst; hydrogenation took place when hydrogen and olefins were passed over the catalyst. The hydrogenation proceeded readily with olefins containing a terminal double bond, while cyclohexene and 2-methyl-2-butene hydrogenated much slower. The hydrogenation was accompanied by a double-bond migration. This hydrogenation is reminiscent of the hydrogenation of ethylene and of the exchange of hydrogen-deuterium over alumina catalyst, which were interpreted as taking place on the intrinsic acidic and basic sites of the catalyst 15-17.

Secondary and primary alcohols underwent dehydrogenation over calcium oxide catalyst (Table 8). *n*-Butyl- and isobutyl alcohol formed the corresponding aldehydes while *sec*-butyl alcohol and pinacolyl alcohol produced 2-butanone and pinacolone, respectively. Calcium oxide from calcium hydroxide which was calcined at 500° seemed to be the most effective catalyst for this reaction. Tertiary butyl alcohol, which cannot dehydrogenate, underwent at 320° a minor

dehydration to isobutylene. The dehydration amounting to 64% occurred however when 2-phenyl-2-propanol was passed over the same catalyst. 2-Phenyl-1-ethanol, which is a primary alcohol, underwent both dehydration and dehydrogenation.

The dehydration of the alcohols might have occurred through a concerted mechanism in which the intrinsic acidic and basic sites which are presumably present in the calcium oxide, participated. These sites could have been formed through imperfections in the crystalline structure of the calcium oxide created by calcination (9) and might be similar to those proposed for the alumina catalysts (18).

Hydrogen transfer reaction between isopropyl alcohol and butanone was one of the most facile reactions of alcohols and had occurred with a conversion of about 40-50% at 320°. Due to the almost equimolar amount of the ketone and alcohol produced, it could be assumed that this reaction proceeded through a concerted mechanism.

A more detailed study of the calcium oxide catalysts and of the reactions would be required in order to establish in more details the mechanism of the action of calcium oxides on hydrocarbons.

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